

PA1220US

PCT

WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

<p>(51) International Patent Classification 6: C08F 4/622, 10/00</p>	<p>A1</p>	<p>(11) International Publication Number: WO 95/04761 (43) International Publication Date: 16 February 1995 (16.02.95)</p>
<p>(21) International Application Number: PCT/US94/08909 (22) International Filing Date: 3 August 1994 (03.08.94) (30) Priority Data: 08/103,505 6 August 1993 (06.08.93) US (71) Applicant: EXXON CHEMICAL PATENTS INC. [US/US]; 5200 Bayway Drive, Baytown, TX 77520 (US). (72) Inventors: JEJLOWO, Moses, Olukayode; 3410 Park Springs, Kingwood, TX 77345 (US). BAMBERGER, Robert, Lee; 15903 Sea Palms Drive, Crosby, TX 77532 (US). (74) Agents: SHER, Jaimes et al.; Exxon Chemical Company, P.O. Box 2149, Baytown, TX 77522-2149 (US).</p>	<p>(81) Designated States: AU, CA, CN, JP, KR, RU, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). Published <i>With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i></p>	
<p>(54) Title: POLYMERIZATION CATALYSTS, THEIR PRODUCTION AND USE (57) Abstract This invention is directed toward the polymerization of olefins, optionally with a comonomer in the presence of metallocene catalyst to produce a polymer product having a controlled molecular weight distribution, ranging from narrow to broad, a high molecular weight and a narrow composition distribution. The catalyst of the invention provides for linear polyethylenes and ethylene-α-olefin copolymers with substantially higher melt strength than linear polyethylenes produced with a conventional Ziegler-Natta catalyst or a typical metallocene catalyst. The invention provides a catalyst for polymerizing olefins comprising a first component comprising at least one transition metal of Group IV, V or VI and bonded to at least two cyclopentadienyl containing rings, said rings each having at least two substituents bonded to each of said rings in the same position; a second component comprising said transition metal and said cyclopentadienyl containing rings, said rings each having at least two substituents bonded to each of said rings in the same or different position than said substituents of said first component; said substituents of the said first and second components can be the same or different, with the provision that when the substituents of said first and second components are the same, said substituents of said components are bonded to said rings in different positions; and a third component comprising said transition metal bonded to said cyclopentadienyl containing rings where one of said rings is substituted identically as said first component and another of said rings is substituted identically as said second component. The invention further provides for catalyst systems comprising the catalyst component above in combination with a cocatalyst and/or activator for the catalyst. The cocatalyst or activator can be either alumoxane or an ionic activator.</p>		

CLAIMS

We Claim:

1. A catalyst system for the polymerization of olefins comprising:
 - 5 a) a catalyst comprising
 - (i) a first component comprising at least one transition metal of Group IV, V or VI and bonded thereto at least two cyclopentadienyl containing rings, said rings each having at least two substituents bonded to each of said rings in the same position;
 - 10 (ii) a second component comprising said transition metal and said cyclopentadienyl containing rings, said rings each having at least two substituents bonded to each of said rings in the same or different position than said substituents of said first component; said substituents of the said first and second components can be the same or different, with the provision that when the substituents of said first and second components are the same, said substituents of said components are bonded to said rings in different positions; and
 - 15 (iii) a third component comprising said transition metal bonded to said cyclopentadienyl containing rings where one of said rings is substituted identically as said first component and another of said rings is substituted identically as said second component; and
 - 20 b) a cocatalyst or activator.
2. The catalyst system of claim 1 wherein said cocatalyst is alumoxane or ionic activator.
- 25 3. The catalyst system of any preceding claim wherein said components are represented by the following formula:

$$B_b(S_sR)_rMD_dA_a$$

wherein R is a cyclopentadienyl containing ring, M is a group IV, V or VI transition metal, S is a hydrocarbyl, alkoxy, silyl, siloxy group or a halogen or two carbon atoms joined together to form a part of a C₄ to C₆ ring; A is a halogen, D is a hydrocarbyl radical, a arylalkyl radical, an alkylidene radical or a hydrocarboxy radical; and B is a radical bridging two R rings, where B contains a carbon, a germanium, a silicon, a phosphorous or a nitrogen atom or combination thereof; r is 2 to 3, b is 0 to 5; s is 2 to 5; d is 0 to 2; a is 0 to 2; and r + d + a is equal to the oxidation state of M.

- 52 -

4. The catalyst system of any preceding claim wherein said catalyst is supported.
- 5 5. The catalyst system of any preceding claim wherein said rings are cyclopentadienyl rings.
6. The catalyst system of any preceding claim wherein said substituents are hydrocarbyl substituents having from 1 to 20 carbon atoms.
- 10 7. The catalyst system of any preceding claim wherein each component is present in an amount greater than 1 mole percent, preferably greater than 5 mole percent.
- 15 8. A process for polymerizing olefins alone or in combination with one or more other olefins, said process comprising polymerizing in the presence of a catalyst system of any one of the preceding claims.
- 20 9. A polymer composition produced by the process of claim 8.
10. A polymer composition comprising a linear olefin polymer having a melt strength greater than 6 cN, preferably 7 cN and a CDBI greater than 50%.
- 25 11. A olefin polymer composition comprising an ethylene and at least one C₃-C₂₀ alpha-olefin polymer having a CDBI greater than 50% and a melt strength greater than $2 + 10/e^{MI}$ where MI is the melt index of the polymer and e is a constant.
- 30 12. A linear olefin polymer composition comprising a polymer having a melt strength greater than $2 + 15/e^{MI}$ where MI is the melt index of the polymer composition and e is a constant.
- 35 13. The composition of any of the preceding claims 9, 10, 11, and 12 wherein the polymer has a MI in the range of 0.01 dg/min to 100 dg/min, preferably 0.5 dg/min to 10 dg/min.

- 53 -

14. The composition of any of the preceding claims 9, 10, 11, 12 and 13 wherein the polymer has a density greater than 0.900 g/cc, preferably greater than 0.910 g/cc to 0.945 g/cc.
- 5 15. The composition of any of the preceding claims 9, 10, 11, 12, 13 and 14 wherein the polymer has I_{21}/I_2 ratio is greater than 14, preferably greater than 18.
16. The composition of any of the preceding claims 9, 10, 11, 12, 13, 14 and 15 wherein the composition has a Mw/Mn greater than 2.2, preferably greater than 4, more preferably greater than 3.5.
- 10 17. A polymeric film produced from the composition of any one of the preceding claims 9, 10, 11, 12, 13, 14, 15 and 16.
- 15 18. The polymeric film of claim 17 wherein said polymer has a density in the range of 0.900 g/cm³ to 0.940 g/cm³, a MWD of greater than 2.6, a CDBI greater than 50%, I_{21}/I_2 greater than 20.
19. The polymer film of claim 18 wherein said polymeric film is a blown film.
- 20 20. A polymeric bag comprising the polymeric film of claims 18 and 19.

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C08F4/622 C08F10/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C08F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP,A,0 283 739 (CHISSO CORP.) 28 September 1988 see abstract; claims; examples see page 7, line 4 - page 8, line 7 ---	1-20
A	WO,A,93 09148 (EXXON CHEMICAL PATENTS INC.) 13 May 1993 see abstract; claims; examples ---	1-20
A	EP,A,0 310 734 (FINA) 12 April 1989 see abstract; claims -----	1-20

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search

11 November 1994

Date of mailing of the international search report

23.12.94

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+31-70) 340-3016

Authorized officer

Mettler, R-M